

Geochemical Characterization of Major and Trace Elements in Coastal Sediments of Gulf of Govatr, Southeastern Iran

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Abstract

Geochemical characteristics of the coastal sediments in Gulf of Govatr (Southeastern Iran) have been investigated by taking 13 sediment samples in the 2012 summer. The samples have been subjected to a total digestion technique and analysed using Inductively Coupled Plasma (ICP)–Mass Spectrometry (MS) for selected major (i.e. Al, Ca, Fe, K, Ti, Mg, Mn and Na) and trace elements (e.g. Ba, Co, Cr, Cu, Pb, Zn, Ni, P and V). The main objectives are to understand the processes controlling major and trace elements to identify natural and anthropogenic sources in the coastal environment using statistically regressed elemental concentrations to establish regional baseline levels. Geochemical maps of major and trace element show that the highest concentrations of this element are related to the Pasabandar coastal sediments so that the element concentrations of Fe, Mn, Pb, Zn and Cr, are 15.3, 53.2, 35.1, 24.4, and 100 times respectively to the normal concentration in the study area. Correlation coefficients indicate that colloids such as iron and manganese hydroxides and clay minerals have great role in the mobility of heavy metals in the study area. High correlation of the chromium, magnesium, nickel, and iron elements show that the source of these elements is weathering of ophiolitic rocks by Bahokalat river and transfer of these elements to the sea.

Keywords: Govatr Gulf, coast sediment, major and trace elements

1. Introduction

Sediments from the marginal marine and near shore environments had been studied by a number of geologists for a considerable period of time to determine the process of deposition of ancient sediments. The nature of sediments is modified by anthropogenic activities and as the impact of these activities has increased more in the following years, sediment geochemistry had been pursued with the objective to assess coastal pollution (Emery, 1960; Shepard et al., 1960; Strakhov, 1961; Van Andel & Shor, 1964; Faganelli et al., 1987; Karbassi & Amirnezhad, 2004; Pekey, 2006; Marchand et al., 2006; Sundararajan et al., 2009). Most of the chemical changes take place at or close to the sediment/water boundary and, for this reason, it is important to study the geochemical composition of bulk sediments (Hirst, 1962; Calvert, 1976). The shores of Gulf of Govatr are unique in Iran for their proximity to the permanent river Bahokalat, complicated estuaries and mangrove forests. In this region, Bahokalat River is the main natural source of elements input. This river passes through varied Makoran zone formations and delivers a wide range of elements into the Gulf of Govatr environment. Major fishing harbors like Pasabandar and Govatr and also shrimp farming ponds in the region can play a major role in human-generated pollution of the environment. In spite of this, and the very important features of the region in terms of unique ecosystems, there have been no environmental studies on variations and distribution of major and trace elements concentrations in the region. The objective of this study is to investigate on the geochemistry of the surficial sediment in Govatr Gulf along the Iranian coast of the Oman Sea. The main objectives are (1) to characterize the behaviour of major and trace elements in the surface sediments; (2) to establish baseline models by means of a normalization method and assess the contribution from natural and anthropogenic sources in the coastal environment; and (3) to evaluate the spatial distribution of major and trace elements in Govatr Gulf.

2. Materials and Methods

2.1 Study Area

The Gulf of Govatr is located at 21° 00' to 21° 20' Northern Latitude and 61° 20' to 61° 40' Eastern Longitude, at the extreme southeastern Iran, 100 km east of Chabahar in Sistan & Beluchestan Province (Figure 1). Half of this gulf is on Iranian side and the other half is on the side of Pakistan. It covers 350 km² area with 8 m average depth and its estuary width is 31 km (from Giovanni Port in Pakistan to Pasabandar in Iran). Geologically, the studied area is located in Makran region which is divided into two outer (seaside) and inner parts. The studied area is in the outer part. Its general features include ophiolite assemblages, sediments with flysch facies, and the exposed rocks that are not earlier than Cretaceous period. The region's ophiolite complexes are mostly narrow and more or less consistent strips that are usually exposed along the main elongated faults. Mc Call (1997) Believes these complexes are part of a larger ophiolite that have been separated recently. Bahokalat River carries the most water in the region and by passing through above rock formations, collects vast waters from southeastern Iran and delivers them to the sea of Oman at the Gulf of Govatr. Therefore, It is expected that a major source of elements in sediments of Gulf of Govatr is erosion of ophiolite rocks by Bahokalat River and their transportation to sea. On the other hand, Gulf of Govatr is unique for its special climatic and geological

features like sea level variations during different geological periods, weathering and erosion processes, and geological activities caused by sinking of Oman tectonic plate and uplifting of Makran plate, and it generally consists of detrital sedimentary rocks. The various rock units at coastal region and seaside lands are: Miocene period marine rocks, Miocene- Pliocene marine and sand rocks, sand/silt sediments of alluvial fans and sediments containing animal exoskeletons.

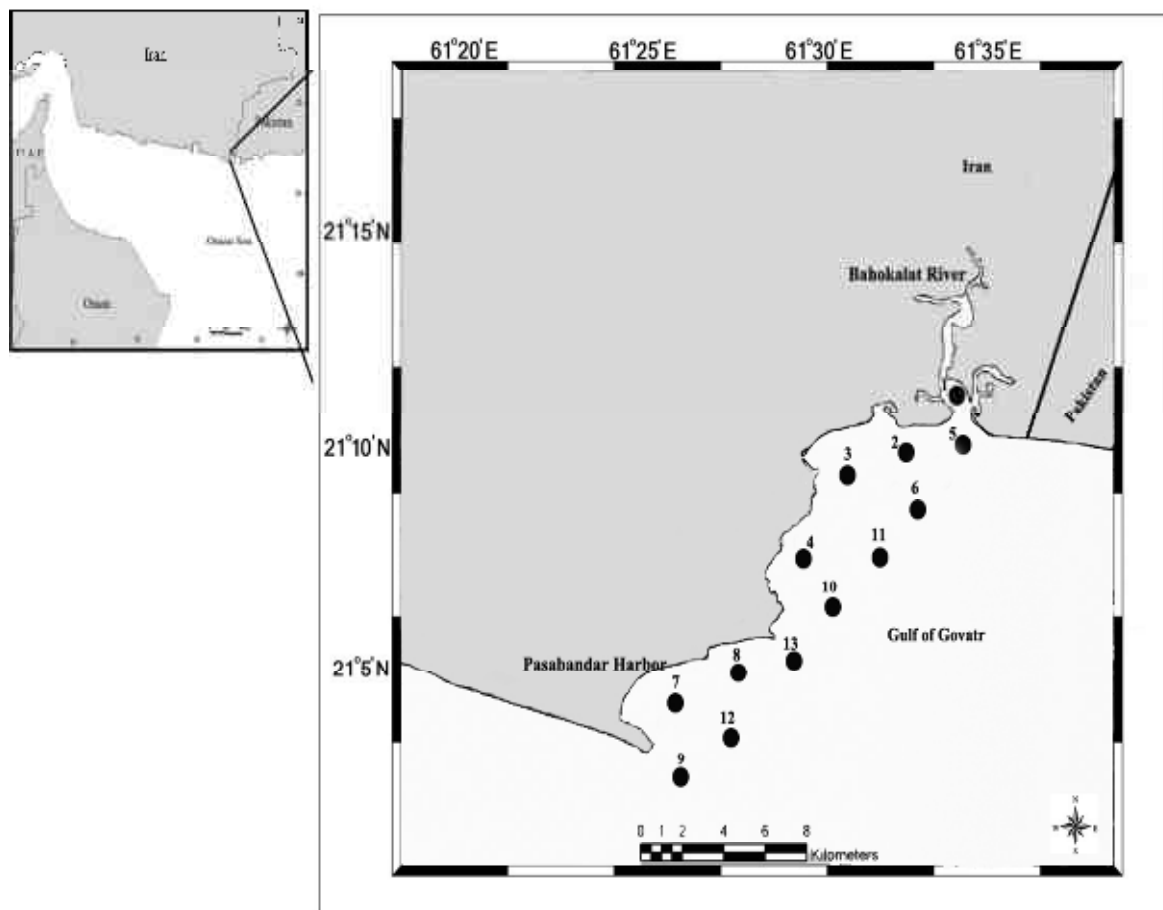


Figure 1. Map of Gulf of Govatr indicating sampling stations

2.2. Sampling and analytical methods

Samples of sediments (about 5–10 cm thickness of the surface sediment with a stainless steel grab sampler during low tide) were collected three times representing different seasons in the 2012 summer from the intertidal zone of 13 stations in the Gulf of Govatr. Sampling location was detected using GPS localisation. All stations are situated in the proximity of different geochemical, hydrological and human impacts. Sediments were dried in the oven at 70 °C then kept in polythylene until analysis (Amini Ranjbar, 1998). Sediment samples of 0.5 g were digested in Teflon vessels for 2 h with a mixture of 3: 2:1 HNO₃, HClO₄ and HF acids, respectively, according to the method described by Origoni and Aston (1984). The metals were analyzed by using Inductively Coupled Plasma (ICP)–Mass Spectrometry (MS) model NexION 350.

3. Results and Discussion

3.1 Sediment granulometry

Granulation studies of sediments show the presence of particles smaller than 2μ, which are generally clay minerals, to coarser particles such as sand and sometimes gravel in the sediments. But the percentage of clay and silt is higher in the studied area sediments as shown in Figure 2. The detrital particles like quartz, feldspar, detrital carbonates, and biochemical particles (mostly bivalve shells) are also found in sediments. Based on sediment size studies, and according to Folk diagram (1974), 7 types of sediments were identified in the Gulf of Govatr, namely: clay, sandy clay, clay loam, sandy/silty clay, silty sand, sandy loam, and sand. Generally, sediments near the coast are mostly sandy, and by getting farther from the coast, the sediments become finer. Coarser particles are mostly animal's thorny exoskeletons. But by distancing from the shoreline and getting nearer to deeper areas, sediments become spherical and the crushed shells do not show sharp edges and thorny

shapes any more. In coastline ridges, high mechanical erosion of coastal rocks caused by waves (particularly in Monsoon seasons) result in very coarse sediments sized like gravel. Finer particles settle in bays between two sides of the cape. The types of wind deposited sediments on the shoreline and Bahokalat River estuary sediments are sandy, and that of Govatr estuary are silt and clay.

Generally, in 97% of studied samples of animal exoskeletons, carbonates were found in 93% of samples, opaque ore in 20% of the samples, plant parts in 50% of the samples, quartz in 90% of the samples, and gravel in all samples (100%). Main biochemical sedimentary parts in the studied area included bivalve shell fragments, gastropods, crushed fragments of crabs, echinoderm thorns, coral parts, annelids, etc. These fragments were mostly seen in abundance in medium to coarse sand fractions, such that the larger the particles size, the higher is the percentage of these fragments. The morphoscopical analysis of particle surfaces shows some seashells are not shiny or have undergone discoloration which is evident by red and dark colors on the surface. The main reason for color diversity of these shells is iron sulfides and organic materials found in the region.

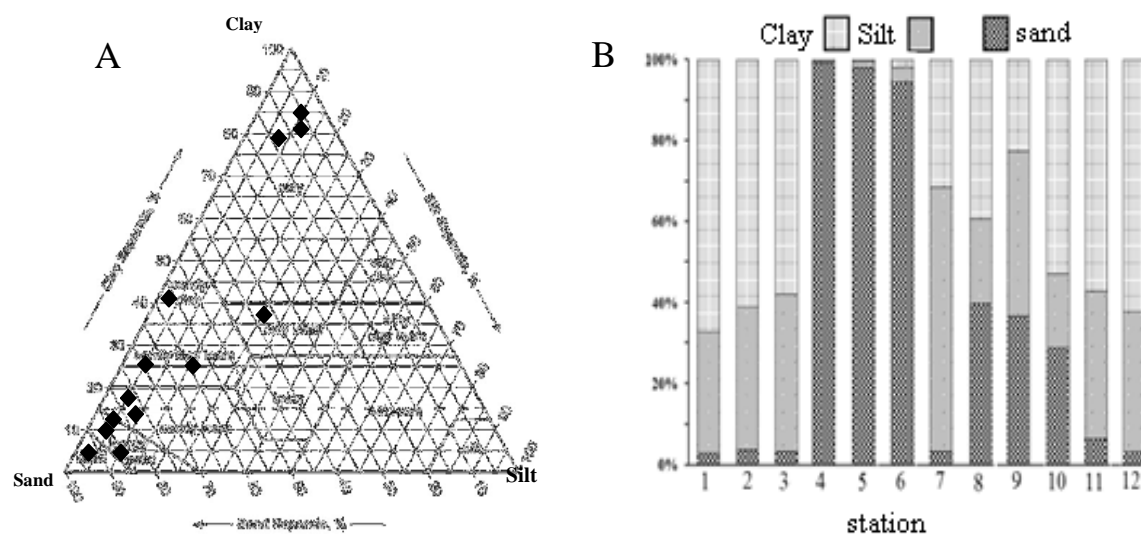


Figure 2. Sediments type in Gulf of Govatr (A), and the frequency percentages of sand, silt, and clay in the study area (B)

3.2 Geochemistry of major and trace elements

The concentrations of major, trace and heavy elements in the studied area sediments are summarized in Table 1. The aluminum concentration variations are between 1.17% to 7.46%. The average concentration of this element in the coastal sediments is almost half of its concentration in the crust, and in all samples its concentration is less than the natural grade of the crust. It is caused by low aluminosilicates content and their weathering products (clay minerals) in the sediments; and abundance of other minerals such as those containing calcium carbonate/sulfate (resulted from animals exoskeletons and detrital particles) in the sediments. High calcium content of sediments (twice that of natural grade in crust) confirms this (Figure 3). High aluminum content of Bahokalat riverbed sediments imply a high clay content in these sediments. The iron, potassium, and magnesium concentration variations are similar to aluminum, i.e. 0.91-7.68, 0.34- 2.39 and 0.64-2.52, respectively. Their concentrations in most samples are less than the crust, and also higher abundance of these elements in finer sediments shows their coherence with clay minerals. Sodium element concentration variations are not too much (0.34-2.54%). Since the sediments were distilled and rinsed twice by distilled water which removed surface salt, as a result the sediment's sodium concentration relates to the geochemistry of the sediments themselves. Among major elements, sulfur showed the highest enrichment relative to crust. This is because of gypsum ore in the coastal region of the studied area. The organic materials abundance in the sediments is another reason for the high concentration. In various geochemical environments, trace elements mostly replace major elements with similar geochemistry according to elements substitution laws. Among such elements, lithium, barium, and rubidium are chemically similar to potassium and usually replace it in clay minerals.

Therefore, like potassium in fine sediments of Pasabandar and Bahokalat riverbed, they show more enrichment. Also, concentrations of barium, rubidium, titanium, and manganese are much less than their average in the crust due to low content of feldspar and clay in the studied area sediments relative to crust. Strontium element fully matches calcium's geochemistry and its concentration variations in the studied area follows calcium variations pattern. Manganese and titanium elements concentration variations are obviously similar to those of Iron. Phosphorus is a nutrient whose concentration is higher at coastal areas that are far from human activities. The

lowest amount of this element is found in non-marine environments such as Bahokalat River. The enrichment diagrams of trace elements also shows higher concentrations of lithium and rubidium near Pasabandar harbor which has high amounts of clay minerals. Manganese and titanium are rare in the region and only show some enrichment at Pasabandar harbor which relates to human pollution. This anomaly is because of transportation of fine metal particles to the shore by high waves in the region. They originate from boat oil disposal in seawater at this port.

Table 1. Concentrations of major and trace elements in coastal sediments collected from the Gulf of Govatr

Element/Sample		1	2	3	4	5	6	7	8	9	10	11	12	13
Al	(%)	4.09	3.54	7.46	3.99	7.18	1.17	2.95	7	6.62	6.22	6.18	3.94	6.62
Fe	(%)	2.44	3.45	4.95	3.06	4.35	0.91	7.68	4.12	4.35	3.84	3.66	2.22	4
Mn	ppm	608	838	611	828	565	283	1540	573	454	669	678	583	616
Mg	(%)	1.23	1.11	2.52	1.19	2.1	0.64	1.07	2.34	2.27	1.9	2.43	1.12	2.18
Ca	(%)	6.11	7.35	3.99	7.35	4.12	15	5.75	3.34	3.43	5.3	3.43	5.87	4.74
Na	(%)	1.34	2.54	1.99	1.53	0.99	0.34	2.2	1.84	2.53	1.79	2	1.58	1.93
K	(%)	1.05	0.87	2.39	1.01	2.24	0.34	0.46	2.19	2.2	1.6	1.79	0.91	2.03
S	(%)	0.05	0.18	0.18	0.07	0.03	0.15	0.08	0.27	0.61	0.06	0.12	0.11	0.19
P	ppm	510	1020	620	860	700	1730	2570	630	720	590	640	1680	830
Ti	ppm	0.22	0.42	0.38	0.34	0.36	0.06	1.67	0.32	0.32	0.35	0.32	0.36	0.34
Cr	ppm	100	1550	92	771	96	15	10000	104	105	94	95	755	113
Li	ppm	27	24	56	27	57	9	19	53	52	43	45	26	52
As	ppm	11	14	9	9	5	3	14	10	6	8	6	5	6
Rb	ppm	54.8	42.7	127	48	123	15.9	20.7	120	114	73.6	90.5	44.2	105
Sr	ppm	251	291	151	268	157	2380	241	138	154	193	143	230	169
Ba	ppm	185	252	215	172	201	109	112	189	191	170	182	142	187
Zn	ppm	41	60	76	50	83	13	174	82	151	58	69	55	74
Sn	ppm	1.9	2.6	2.6	2.1	2.7	0.7	2.3	2.1	3	1.3	1.7	1.3	2
Pb	ppm	13.9	18.8	16.5	14	14.7	7.3	25.8	16.9	16	12.8	13.5	11.5	13.6
Ni	ppm	50.6	66.4	97.8	63	109	14.9	72.2	104	101	79.6	92.6	49.1	92
Cu	ppm	19.4	46.4	39.4	19.6	25.7	6.2	19.4	32	101	27.5	29	15.6	25.8
Sb	ppm	0.37	0.55	0.43	0.44	0.44	0.21	0.97	0.49	0.41	0.43	0.46	0.4	0.38
Bi	ppm	0.18	0.18	0.32	0.17	0.33	0.11	0.26	0.26	0.23	0.22	0.28	0.14	0.24
Mo	ppm	0.59	2.23	0.4	1.56	0.3	0.26	2	0.61	1.59	0.31	0.42	0.63	0.4
Co	ppm	14.2	20.5	25.7	17.3	23.1	4.9	53.2	23.8	20	17.8	20.7	14.9	20.5
Cd	ppm	0.12	0.15	0.11	0.19	0.13	0.15	0.12	0.11	0.33	0.09	0.09	0.08	0.13
pH		8.13	8.13	8.12	8.11	8.13	8.15	8.11	8.16	8.13	8.12	8.13	8.14	8.11
Temp.	°C	30.1	30.2	29.8	31.1	30.1	30.4	30.7	30.1	29.9	30.3	30.1	30.2	30.1

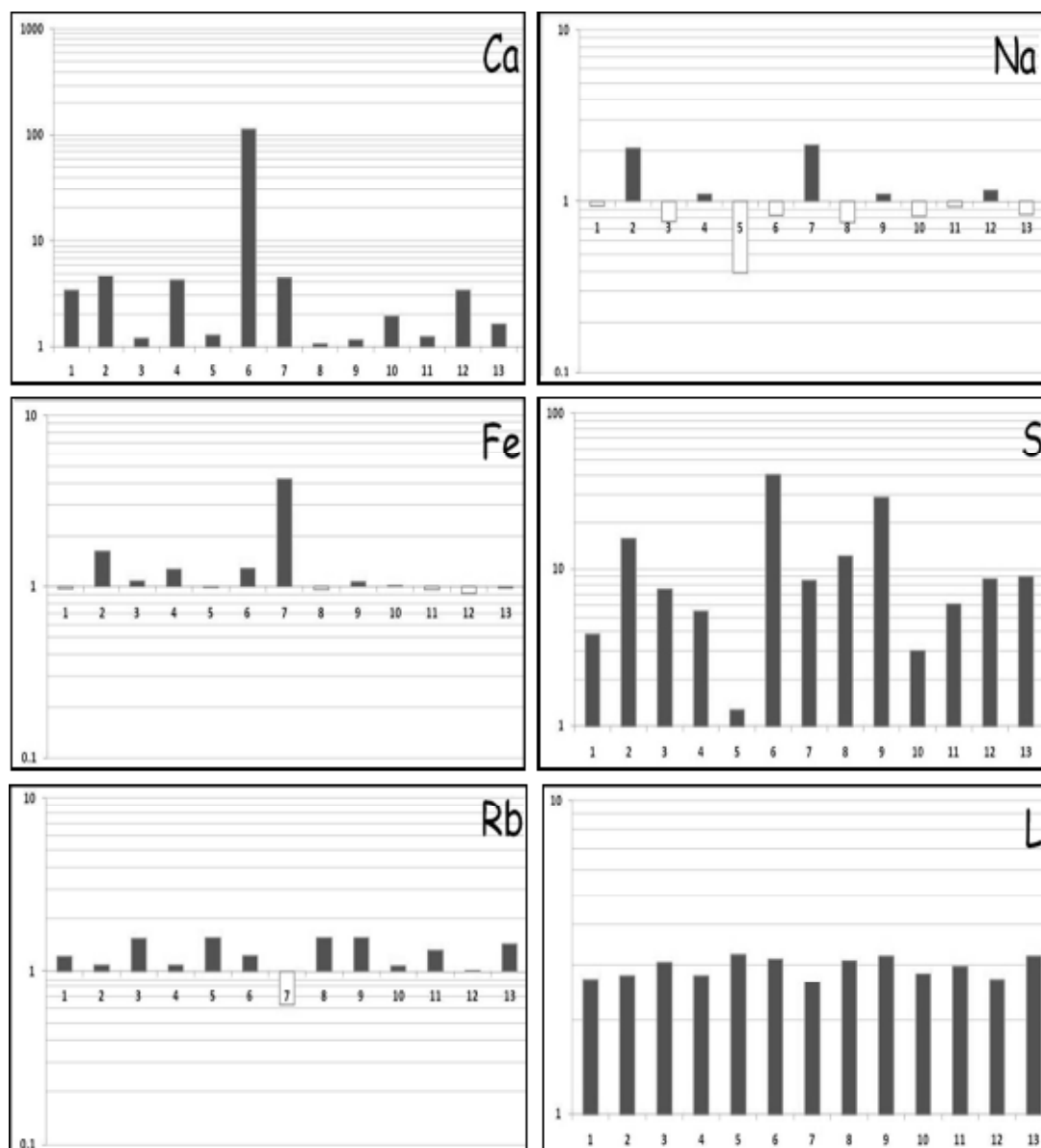


Figure 3. Enrichment diagram of some major and trace elements (Ca, Na, Fe, S, Rb, Li) relative to the crust of earth

3.3 Geochemistry of heavy metals

Table 1 shows heavy metal concentrations in the Gulf of Govatr. It shows that the heavy metal concentrations in natural coastal areas is similar to their average amount in crust or less (except for Cr, As and Sb). Cr concentration is mostly higher at coastal area for its high specific gravity. As a result, its concentration is high in coarse coastal sediments but lower in loam sediments. The As concentration is generally high in the region since this element is more soluble in seawater relative to other toxic elements and it is inclined to get enriched in evaporates minerals. Based on enrichment diagrams in fig.4, heavy metals concentrations in most samples taken from Pasabandar harbor and its intertidal zone at eastern shore are more than their natural concentration. Elements such as Cd, Co, Pb, Sb, Sn, Cr, Cu, Ni, Zn and As show high concentration levels in Pasabandar. These variations are caused by finer grain of Pasabandar harbor coastal sediments and higher level of pollutants entering the above harbor because of higher number of fishing boats. In sample 7 taken from Pasabandar shore's sandy sediments, concentrations of elements such as Fe, Mn, Pb, Zn and Cr are 3.15, 2.35, 1.35, 4.24 respectively, which are 100 times more than their natural concentration in the study area.

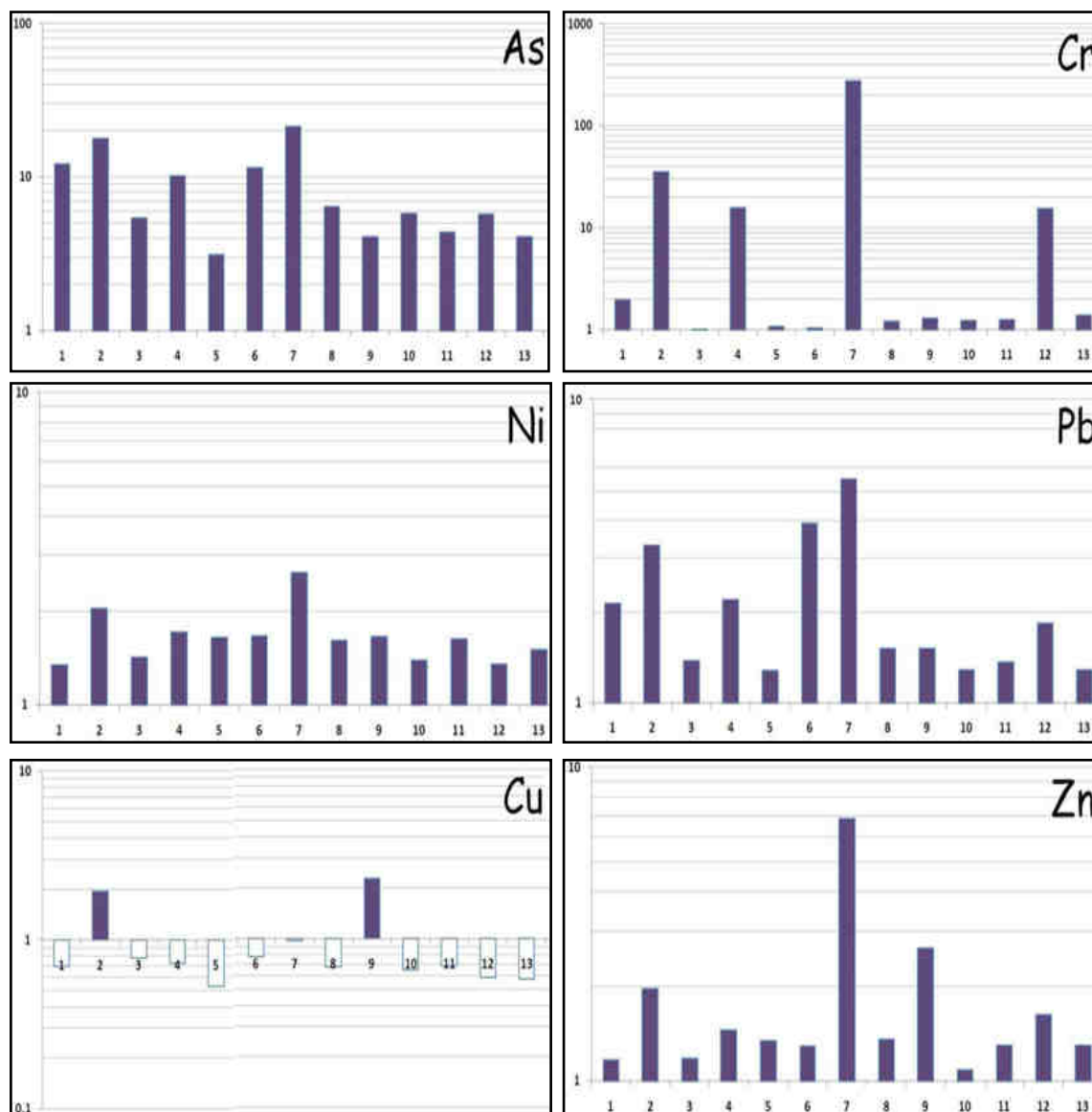


Figure 4. Enrichment diagram of heavy metals (Cr, Pb, Ni, Zn, Cu, As) relative to the crust of earth

3.4 Correlation coefficient

The elements correlation coefficient diagrams show high correlation among elements in the Gulf of Govatr. This can be attributed to a common pollution source or similar geochemistry, e.g. chalcophile elements show similar concentration increase trend. Also, Fe and Mn follow a fully similar concentration increase pattern with a correlation coefficient of ~ 0.7 . The uniform increase of Fe and Mn along other heavy metals is a result of absorption of these elements in the hydroxides of these two elements. Fe shows a close correlation with many elements such as As, Co, Cu, Sb, Zn, Bi, Sn, Mo, Mn and Pb. This is because of absorption of these elements by iron hydroxide colloids. High correlation of Cr, Mn, Fe and Mg can be caused by input of these elements through weathering of Ophiolite rocks along the Bahokalal River. Another reason could be the common source of pollution of some of these elements with Fe (e.g. Sn, Cu, Zn) or their similar geochemistry with Fe (Co and Mn). This is also true for Mn, there is a high correlation between Mn and heavy metals. The amount of Al in sediment samples is a sign of clay minerals quantity. Therefore, the correlation of elements with Al can be used as a sign of correlation between these elements with clay minerals quantity. Another important point is the high correlation of Cu, Ni, Zn and Pb, with the clay quantity in samples. High correlation of clay with Fe and specially Mg ($r=0.91$) is a result of presence of these elements in clay minerals structures. The amount of clay minerals as particles that efficiently absorb heavy metals is very important. The negative correlation between Ca and other elements imply reluctance to substitute formations containing Ca (except a few trace elements that have similar geochemistry with it). Among study heavy metals, Cd has no significant correlation with other elements for its low concentration and not being introduced through pollution. Here, the highest correlation is

observed between Zn and Ni ($r=0.93$) and Zn and Cu ($r=0.80$). Since organic carbon is a major constructor of marine colloids, the relationship between metals frequency and organic carbon is noteworthy. If metals are connected to organic ligands, a correlation is expected between metal concentration and organic carbon (OC). Table 2 data shows the high correlation between Pb and sedimentary organic carbon ($r=0.6$). This correlation is lower for Ni and Cu. Data showed that there is a low correlation between these elements and S. This points to natural sources of S in sediments while these elements mostly originate from human pollution.

Table 2. Correlation coefficient between elements, clay minerals, and organic carbon in the Gulf of Govatr

	Clay	OC	Cd	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Zn
Clay	1											
OC	0.02	1										
Cd	0.01	0.02	1									
Cr	-0.44	-0.01	0.01	1								
Cu	0.66	0.3	0.05	0.55	1							
Fe	0.51	0.1	0.01	0.93	0.9	1						
Mg	0.91	0.17	0.08	0.58	0.86	0.78	1					
Mn	-0.47	-0.13	0.02	0.91	0.61	0.57	-0.52	1				
Ni	0.89	0.43	0.11	0.65	0.77	0.9	0.82	0.05	1			
P	-0.38	-0.01	0.03	0.11	-0.2	-0.48	-0.4	0.89	-0.23	1		
Pb	0.37	0.6	0.02	0.65	0.75	0.86	0.23	0.77	0.43	0.8	1	
Zn	0.53	0.04	0.01	0.39	0.8	0.91	0.73	0.85	0.93	0.58	0.78	1

Table 3 compares concentration variations of some selected elements in the Gulf of Govatr with similar research in other countries. According to table, Al and As concentration levels in the Gulf of Govatr are similar to other parts of the world. Cd concentration is lower than many other ports. Cu, Zn, Ni and Sn pollution is comparable to most polluted ports around the world. While Pb level in Ramin and Pasabandar ports is low, pollution by this element at Beris Port is 7 times more than Boston Port in the USA. Cr level is abnormal relative to other places. while Alexandria Port in Egypt is the most polluted port in this table, Cr level in the Gulf of Govatr is over 3.5 times more than Cr level in that polluted port.

Table 3. Comparing concentrations of some of the studied elements in the Gulf of Govatr with some Iranian or overseas ports

Location	Pb (ppm)	Ni (ppm)	Cd (ppm)	As (ppm)	Sn (ppm)	Reference
Gulf of Govatr	7.3-15.08	17.9-109	0.08-0.33	3-14	0.7-3	Present study
Iran (Beris harbor)	11.7-1780	31.6-94.9	0.01-0.16	5-12	0.9-524	Hamzeh et al., 2012
Iran (Ramin harbor)	12.6-42.3	39.1-85.2	0.04-1.5	4-10	0.9-7.8	Hamzeh et al., 2012
Egypt (Alexandria)	38-1070	13-53	0.61-2.44	-	-	Mostafa et al., 2004
Spain (Pasajes)	45-346	17-99	1.2-6.4	-	-	Legorburu et al., 1991
Guam (Arpa)	142-395	22.6-51.2	3.5-6	-	31-143	Belt, 1994
Ireland (Cork)	14-23	11-33	< 0.1	-	-	Berrow, 1991
England (Portsmouth)	49-114	-	0.5-3.3	-	-	Soulsby et al., 1987
U.S.A. (Boston)	18-263	8-91	-	-	-	Mostafa et al., 2004
Fiji (Suva)	19.3-272	17-38	0.74-3.04	0.7-45	-	Naidu et al., 1994
Australia (Kembla)	151-484			14-46	-	He et al., 2001

4. Conclusion

The geochemistry of main elements showed that the amount of these elements in the Gulf of Govatr is comparable with the natural concentrations of the earth crust. The Al correlation (as a sign of clay minerals existence) with Ca in the area is negative. Among main elements, S is enriched relative to average content in the crust which is caused by Ca and S bearing minerals in samples. Increasing concentrations of elements such as Li, Ba and Rb in Pasabandar fishing harbor relates to substitution of K by these elements in clay minerals. The concentrations of most toxic trace elements in natural coastal areas were similar to their average level in the crust or less (except Cr and As). Cr has a high specific gravity and thus, it is more concentrated at shores. Therefore, its concentration is high in coarse coastal sediments and low in loam sediments. Generally, As concentration are high in the Gulf of Govatr, since this element is more soluble in seawater relative to other heavy metals and it is inclined to get enriched in evaporates minerals. Correlation coefficient diagrams show increasing concentrations of elements such as Be, Bi, Co, Cr, In, Nb, Ta, Ni, W, Tl, Pb, Sb and Sn in Pasabandar harbor. This is because Pasabandar harbor coastal sediments are fine and the pollutants input is high based on the number of fishing

boats. Correlation coefficients show that there is very high correlation among elements with similar geochemistry or pollution source. Also, the diagrams imply high correlation between Al and most trace elements (based on absorption of these elements by clay minerals), relatively high correlation between Fe and trace elements (based on absorption of these elements by iron hydroxides), and negative correlation between Ca and trace elements (based on trace elements decline to be present in calcium carbonate minerals).

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